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R&T Code 4135017

Technical Report No. 14

*Molecular Recognition in the Oxidation of Catechols  
by Dicobalt-BISDIEN Dioxygen Complexes*

by

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To Be Submitted to

*Journal of Coordination Chemistry*

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January 30, 1992

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CLASSIFICATION OF THIS PAGE

## REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

1. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION / AVAILABILITY OF REPORT Distribution unlimited	
3. CLASSIFICATION / DOWNGRADING SCHEDULE		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
5. NAME OF PERFORMING ORGANIZATION Texas A&M Research Fdn.		6b. OFFICE SYMBOL (If applicable)	
6. ADDRESS (City, State, and ZIP Code) Box 3578 College Station TX 77843		7b. ADDRESS (City, State, and ZIP Code) Department of the Navy Arlington VA 22217	
8. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-88-K-0451	
9. ADDRESS (City, State, and ZIP Code) Department of the Navy Arlington VA 22217		10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. PROJECT NO. TASK NO. WORK UNIT ACCESSION NO.	
11. TITLE (Include Security Classification) Molecular Recognition of O-BISDIEN and Its Dinuclear Complexes			
12. PERSONAL AUTHOR(S) F. S. Cezar, B. Szpoganicz and A. E. Martell			
13. TYPE OF REPORT Technical		14. DATE OF REPORT (Year, Month, Day) 1.30.92	
13b. TIME COVERED FROM TO		15. PAGE COUNT	
16. SUPPLEMENTARY NOTATION To be submitted to Journal of Coordination Chemistry			
17. COSATI CODES FIELD GROUP SUB-GROUP		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) molecular recognition, cobalt dioxygen complex, macrocyclic ligand, 4-methylcatechol, 3,5-ditertiarybutyl catechol, redox reaction, host-guest interaction	
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20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22. NAME OF RESPONSIBLE INDIVIDUAL Ronald D. De Marco		22b. TELEPHONE (include Area Code) 22c. OFFICE SYMBOL (202) 696 5075	

**Molecular Recognition in the Oxidation of Catechols by Dicobalt-BISDIEN  
Dioxygen Complexes**

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**Keywords:**

molecular recognition, cobalt dioxygen complex, macrocyclic ligand, 4-methylcatechol, 3,5-ditertiarybutyl catechol, redox reaction, host-guest interaction

**Abstract**

Formation and degradation of molecular species of the substrate-receptor complex ( $\mu$ -4-methylcatechol)( $\mu$ -peroxo-dicobalt(III)-BISDIEN) were studied by UV-vis spectroscopy. The family of absorbance curves show an intense charge transfer band with a maximum at 367 nm. The degradation redox reaction showed first order behavior. The reactive intermediate has a peroxo bridge and a bridging substrate, 4-methylcatechol coordinated to the two metal centers in the macrocyclic cavity. In the presence of excess substrate and dioxygen, the reaction is catalytic and the product is 3-methyl- *cis,cis*-muconic acid, which was separated by HPLC and characterized by mass spectrometry. When 3,5-di-*t*-butylcatechol was used in place of 4-methylcatechol the redox reaction was not observed. This substrate cannot coordinate to the bimetallic center in the cavity of BISDIEN, and is not oxidized. The results are discussed on the basis of the selectivity of the receptor complex.

## Introduction

Macrocyclic ligands, **1**, having two chelating subunits can form both mono- and binuclear complexes with metallic cations (**2** and **3**). The distance and the spacial arrangement of the two metal centers are determined by the structure of the macrocycle, and with appropriate macrocycles, *receptor-substrate complexes* (also called *cascade complexes*) are formed by subsequent coordination of a bridging substrate bonding to the two metal centers, **4** (Figure 1).<sup>1</sup>

The macrocyclic ligand 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane (BISDIEN), **5**, is a bichelating macrocycle containing two diethylenetriamine units connected by two diethylene oxo ether chains. It forms binuclear complexes with the first row transition metals, and these complexes can act as receptors for bidentate anions bridging two metal centers in the cavity of the macrocycle.<sup>2,3</sup> In this case the binuclear complexes are called *receptors* (or *hosts*) and the bridging anions are the *substrates* (or *guests*).<sup>4</sup>

Formation of a binuclear complex with a bridging oxalate, ( $\mu$ -hydroxo)( $\mu$ -oxalato)( $\mu$ -peroxo)dnicobalt-BISDIEN and subsequent oxidation of the oxalate anion has been reported.<sup>5</sup> Recently, equilibrium studies on catechol-bridged binuclear cobalt(II)-BISDIEN dioxygen complexes were described.<sup>6</sup> Catechol bridges two cobalt centers in the cavity of the macrocycle BISDIEN as in **6**, together with two other bridging ligands,  $\mu$ -peroxo and  $\mu$ -hydroxo. The close proximity of the oxidant and reductant, as well as their simultaneous coordination to the two metal centers, is expected to lead to a facile redox reaction.

## Experimental

**Materials.** The BISDIEN.6HBr employed was synthesized by a modification of the method previously described.<sup>6</sup> 4-Methylcatechol, 3-5-di-*t*-butylcatechol, potassium chloride (supporting electrolyte), and cobalt(II) chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) were reagent grade materials and were used without further purification. The stock solution of cobalt(II) was standardized by titration with EDTA and murexide as indicator.<sup>7</sup>

**Spectrophotometric Studies.** Uv-visible measurements were carried out with a Hewlett Packard 8450 diode array spectrophotometer, equipped with a thermostated cell compartment. Cells of 1.000 cm

path length were used, with the reference containing 0.100 M KCl. Samples of about 0.010 mmol of BISDIEN, 0.0196 mmol of Co(II), and 0.010 mmol of 4-methylcatechol or 3,5-di-*t*-butylcatechol were diluted to 100 mL of solution, and 50 mL were transferred to a sealed thermostated vessel at  $25.0 \pm 0.10$  °C. The p[H] ( $p[H] = -\log [H^+]$ ) values of solutions were adjusted by addition of small volumes of 2 M KOH or 2 M HCl with a Gilmot microburet attached to a thermostated vessel. The experimental vessel was also fitted with glass and reference electrodes, and gas inlet and outlet tubes. The dioxygen complex was allowed to form at 25.0 °C and about 3.5 mL of solution were taken at intervals of time to measure the absorbance.

## Results and Discussion

Following the suggestion presented in Figure 1, the formation of ( $\mu$ -hydroxo)( $\mu$ -4-methylcatecholato)( $\mu$ -peroxo)dicobalt-BISDIEN is shown in Scheme 1. Coordination of a Co(II) ion in one pocket of BISDIEN yielding **7** is followed by coordination of a second Co(II) ion forming the binuclear species **8**. Dioxygen coordinates to the two Co(II) ions, and a hydroxyl ion also bridges the two metal centers, as in **9**. Each cobalt ion is assigned a formal charge +3 and dioxygen is indicated as a peroxo bridge.<sup>2</sup> The complex ( $\mu$ -hydroxo)( $\mu$ -peroxo)dicobalt-BISDIEN behaves as a *receptor* for the substrate 4-methylcatechol to form ( $\mu$ -hydroxo)( $\mu$ -4-methylcatecholate)( $\mu$ -peroxo)dicobalt-BISDIEN, **10**.

Degradation of ( $\mu$ -hydroxo)( $\mu$ -methylcatechol)( $\mu$ -peroxo)dicobalt-BISDIEN is too rapid to allow potentiometric equilibrium studies. On the other hand, with catechol instead of 4-methylcatechol the reaction is slow enough for such studies. The dioxygen complexes formed in the catechol- and Tiron-bridged binuclear Co(II)-BISDIEN systems were studied and the species were characterized potentiometrically.<sup>6</sup> Figure 2 shows the distribution curves of the 1:2:1 BISDIEN:Co(II):catechol system under oxygen as a function of  $-\log [H^+]$ . The dihydroxo species predominates at p[H] values above 11.0. The relative concentration of this species decreases as the p[H] decreases while the concentration of the monohydroxo species increases, reaching a maximum at p[H] 8.8, at which it is 67.0% formed. Protonation of this species yields the bivalent complex,  $Co_2O_2LCat^{2+}$ , which is formed with a maximum at p[H] 7.9. Two other protonated species,  $Co_2O_2HLCat^{3+}$  and  $Co_2O_2H_2LCat^{4+}$ , are formed at lower p[H] values. The species distribution curves in Figure 2 were used as analogs of the 4-methylcatechol complexes and to

Interpret the kinetics of degradation of  $\mu$ -4-methylcatecholato,  $\mu$ -peroxo binuclear Co(II)-BISDIEN complexes.

Formation of  $\mu$ -4-methylcatecholato,  $\mu$ -peroxo binuclear Co(II)-BISDIEN complexes were followed by UV-vis spectroscopy at 25.0 °C, and about two hours were allowed for complete formation of the complex under an oxygen atmosphere. After that, the temperature was increased to 50.0 °C under a nitrogen atmosphere, and degradation of these complexes was followed. Figure 3 shows a family of UV-vis curves with maxima at 367 nm. Intense charge-transfer absorption bands in the 350-400 nm range are characteristic of dioxygen complexes. A plot of  $\log(A-A_0)$  vs time gave straight lines, indicating first-order behavior. Figure 4 shows the graphical determination of the rate constant at p[H] 10.14 and 50.0 °C, to give the value  $6.0 \times 10^{-3} \text{ s}^{-1}$ . Constants obtained at other pH values are presented in Table I.

The contribution of each protonated and deprotonated species of 4-methylcatechol-bridged binuclear Co(II)-BISDIEN dioxygen complexes were determined by equation (1) and the distribution curves of Figure 2.

$$k_{\text{obs}}[\text{complex}] = k_1[\text{Co}_2\text{O}_2\text{H}_2\text{LCat}^{4+}] + k_2[\text{Co}_2\text{O}_2\text{HLCat}^{3+}] + k_3[\text{Co}_2\text{O}_2\text{LCat}^{2+}] + k_4[\text{Co}_2\text{O}_2(\text{OH})\text{LCat}^+] + k_5[\text{Co}_2\text{O}_2(\text{OH})_2\text{Cat}^0] \quad (1)$$

$\text{Co}_2\text{O}_2\text{H}_2\text{LCat}^{4+}$  and  $\text{Co}_2\text{O}_2\text{HLCat}^{3+}$  are protonated forms of 4-methylcatechol-bridged binuclear Co(II)-BISDIEN dioxygen complexes;  $\text{Co}_2\text{O}_2\text{LCat}^{2+}$  is the bivalent form, and  $\text{Co}_2\text{O}_2(\text{OH})\text{LCat}^+$  and  $\text{Co}_2\text{O}_2(\text{OH})_2\text{Cat}^0$  are hydroxo complexes. The specific rate constants determined are reported in Table II. The reactivity of each complex species are of the same order of magnitude, and for the two protonated forms were assumed to be the same. The results are reasonable in that all species have a peroxo bridge and the substrate bridged to the two metal centers. The small differences in the reactivity of each species could be due to conformational differences, and the presence of an additional coordinating group in the hydroxo complexes.

An experimental solution containing BISDIEN, Co(II), and an excess of 4-methylcatechol and oxygen were allowed to react completely to transform all substrate into the reaction product. The product, as a result of an oxidation reaction, could be an *ortho*quinone as in 11, or an open chain product such as

the *c/s*, *c/s*-muconic acid, **12**. Three mass spectra were taken from the product separated by HPLC. All three showed a peak at  $m/z = 219$  is identified as  $[m + Cu]^+$  where Cu is from the probe.

The results indicate that in an excess of substrate and oxygen, the reaction is catalytic and the product is the open chain 3-methyl-*cis,cis*-muconic acid. No attempt was made to see which isomer is formed but in the oxidation of catechol by the enzyme pyrocatecase the product is *cis,cis*-muconic acid.<sup>8-11</sup>

The proposed mechanism for the oxidation of 4-methylcatechol in the cavity of BISDIEN is shown in Scheme II. Dioxygen and 4-methylcatechol coordinate to the two metal centers in the cavity of BISDIEN forming  $(\mu\text{-4-methylcatechol})(\mu\text{-peroxo})\text{dicobalt-BISDIEN}$ , **13**, in which one electron of each  $\text{Co}^{2+}$  is transferred to the dioxygen to form a peroxo-bridge. The two electron transfer from the substrate to the metal centers yields **14**, which is followed by oxygen insertion and bond breaking forming 3-methylmuconic acid and binuclear  $\text{Co(II)-BISDIEN}$ . Further coordination of another dioxygen molecule and 4-methylcatechol closes the catalytic circle.

**Molecular Recognition.** When 3,5-di-*t*-butylcatechol was used in place of 4-methylcatechol, the oxidation reaction was expected to occur faster, since the presence of two *t*-butyl radicals bonded to the aromatic ring makes the oxidation of this substrate much easier than 4-methylcatechol or catechol itself. However, the oxidation reaction was not observed or was too slow when 3,5-di-*t*-butylcatechol was used instead of 4-methylcatechol. HPLC revealed formation only of the  $(\mu\text{-hydroxo})(\mu\text{-peroxo})\text{dicobalt-BISDIEN}$ , with 3,5-di-*t*-butylcatechol uncoordinated. The detection of  $(\mu\text{-3,5-di-}t\text{-butylcatechol})(\mu\text{-peroxo})\text{dicobalt-BISDIEN}$  by potentiometric titration also failed. This species does not form, or its concentration is too small to be detected by this technique.

Although 3,5-di-*t*-butylcatechol is a better reducing agent than 4-methylcatechol, it does not undergo oxidation because it cannot coordinate to the two metal centers of the *host* complex. Since all the dioxygen in the deaerated solution is present as a  $\mu\text{-peroxo}$  group, bridging the two cobalt centers in the cavity of BISDIEN, the oxidation reaction requires the substrate to be coordinated to the metal centers.

### Acknowledgement

This research was supported by the Office of Naval Research and by (Brazil).



## References

1. J. M. Lehn, *Pure Appld. Chem.*, **52**, 2441 (1980).
2. R. J. Motekaitis, A. E. Martell, J. P. Lecompte and J. M. Lehn, *Inorg. Chem.* **22**, 609 (1983).
3. P. K. Coughlin, S. J. Lippard, A. E. Martin and J. R. Bukowski, *J. Am. Chem. Soc.* **102**, 7616 (1981).
4. J. M. Lehn and P. G. In "*Progress in Macrocyclic Chemistry*", R. M. Izatt and J. J. Christensen (Eds.), (John Wiley & Sons, New York, 1987), Vol.3.
5. R. J. Motekaitis and A. E. Martell *J. Am. Chem. Soc.*, **110**, 8059 (1988).
6. B. S. Szpoganicz, R. J. Motekaitis and A. E. Martell, *Inorg. Chem.*, **29**, 1467 (1990).
7. G. Schwarzenbach and H. Flaschka, *Complexometric Titration* (Methuen Co., London 1969), p. 244.
8. M. Nozaki, In "*Molecular Mechanisms of Oxygen Activation*", O. Hayaishi (Ed.), (Academic Press, New York, 1974), p. 135.
9. O. Hayashi and K. Kashimoto, *J. Biochem. (Tokyo)*, **37**, 371 (1950).
10. O. Hayaishi, M. Katagiri and S. Rothberg, *J. Am. Chem. Soc.*, **77**, 5450 (1957); *J. Biol Chem.*, **229**, 905 (1957).
11. Y. Kojima, N. Itada and O. Hayaishi, *J. Biol Chem.*, **236**, 8 (1961).
12. J. Tsuji and H. Takayanagi, *J. Am. Chem. Soc.*, **13**, 7349 (1974).

## Figure Captions

- Figure 1 Sequential formation of a cascade complex involving complexation of two metal cations to yield a binuclear macrocyclic complex, followed by coordination of a bridging substrate to the two metal centers.
- Figure 2 Species distribution curves of the 1:2:1 BISDIEN:Co(II):catechol system under oxygen as a function of  $-\log [H^+]$ , for a solution initially containing  $1.00 \times 10^{-4}$  M catechol under oxygen ( $P_{O_2} = 1$  atm), where  $Co_2O_2LCat^{2+}$  is the bivalent species of catechol bridged binuclear cobalt(II)-BISDIEN dioxygen,  $Co_2O_2(OH)LCat^+$  and  $Co_2O_2(OH)_2LCat^0$  are the mono- and dihydroxo species, respectively, and  $Co_2O_2HLCat^{3+}$  and  $Co_2O_2H_2LCat^{4+}$  are the mono and diprotonated species.
- Figure 3 Absorption spectra illustrating the degradation of the 4-methyl-bridged binuclear Co(II)-BISDIEN dioxygen complex at 50.0 °C;  $\mu = 0.100$  M KCl.  $[BISDIEN] = 1.00 \times 10^{-4}$  M,  $p[H] = 10.14$ .
- Figure 4 First order plot for degradation of the 4-methyl-bridged binuclear Co(II)-BISDIEN dioxygen complex at  $p[H] 10.14$  and 50.0 °C.
- Figure 5 Mass spectra of 2.65 mg of the product of oxidation of 4-methylcatechol; (a) is in DTT/DTE with NaI matrix, (b) is in 3-NBA/LiI matrix, and (c) is in 3-NBA/KI matrix. The molecule is  $C_7H_8O_4$  and molecular weight is 156;  $(m + Cu) = 219$ .

Fig. 1

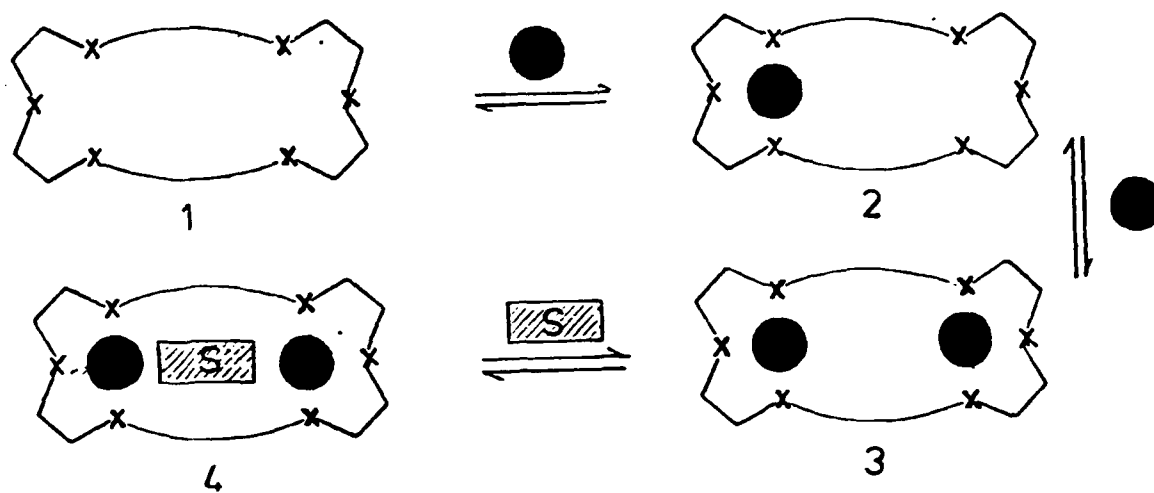


Fig.2

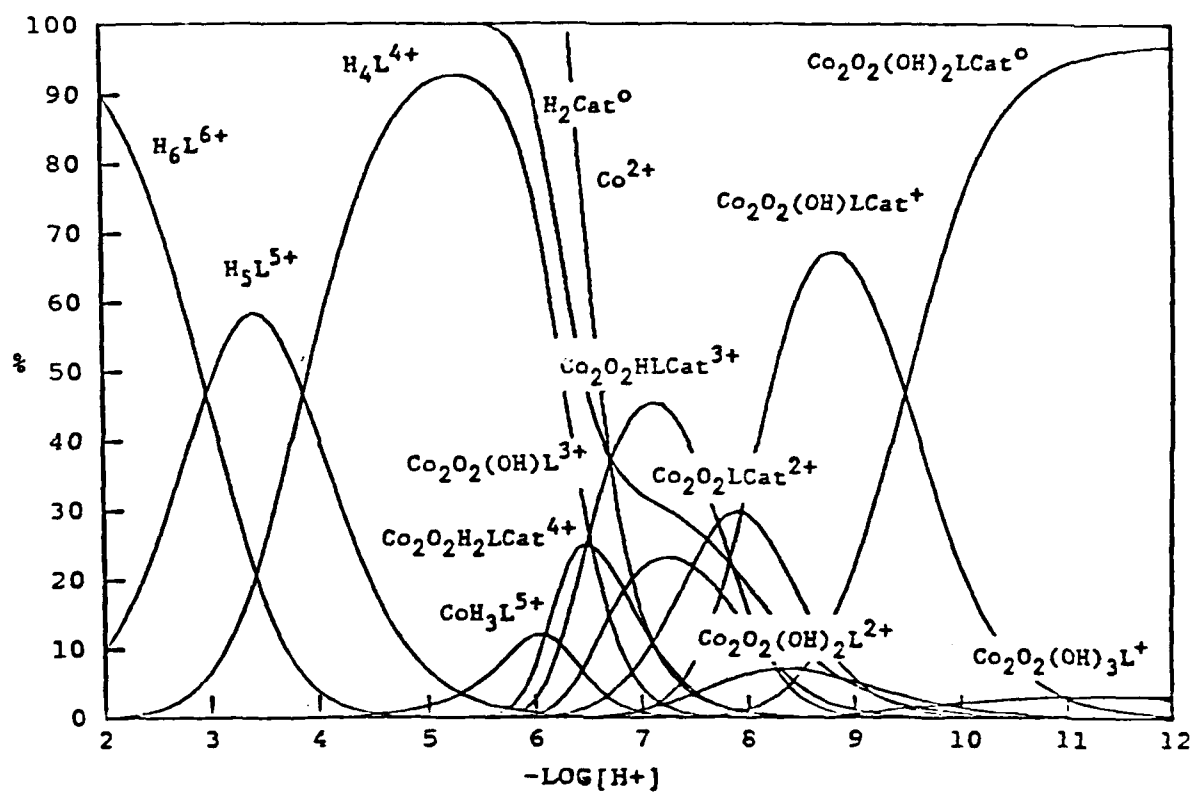


Fig.3

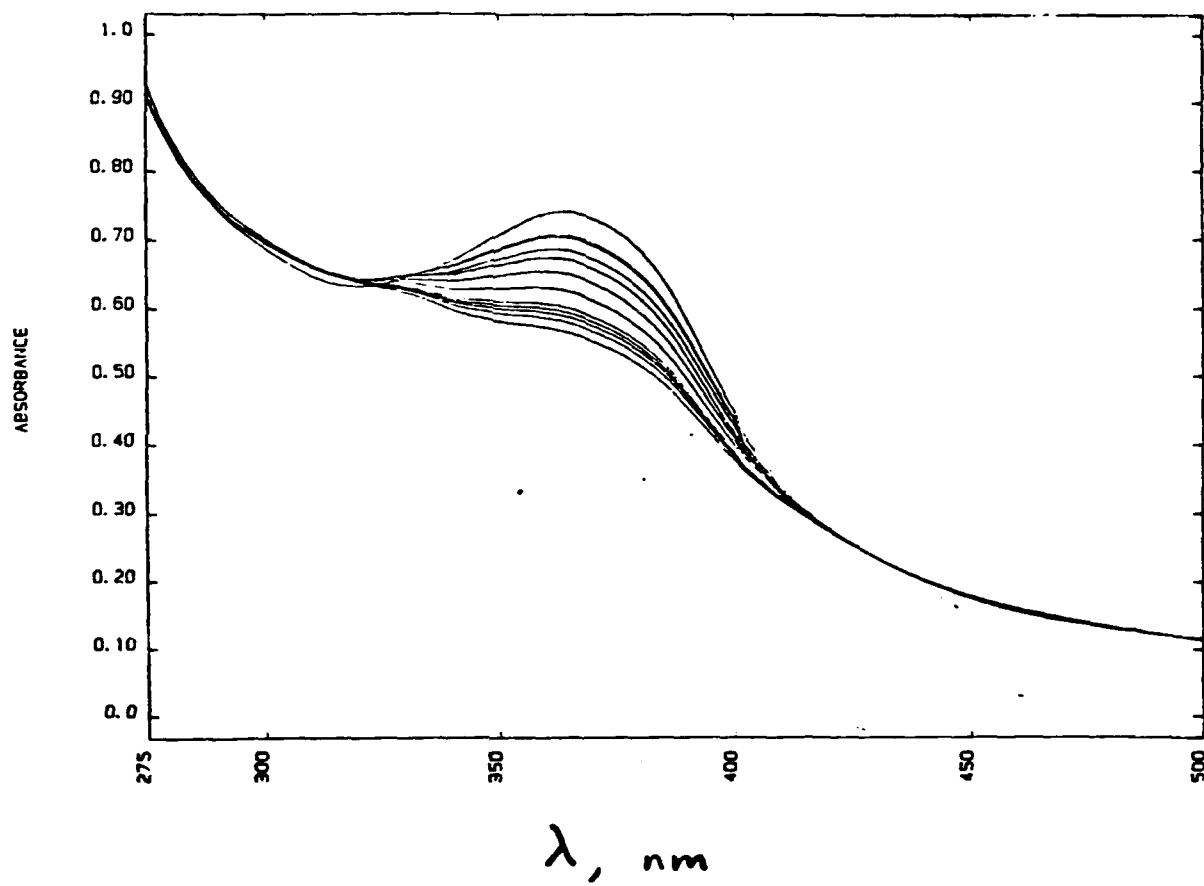


Fig.4

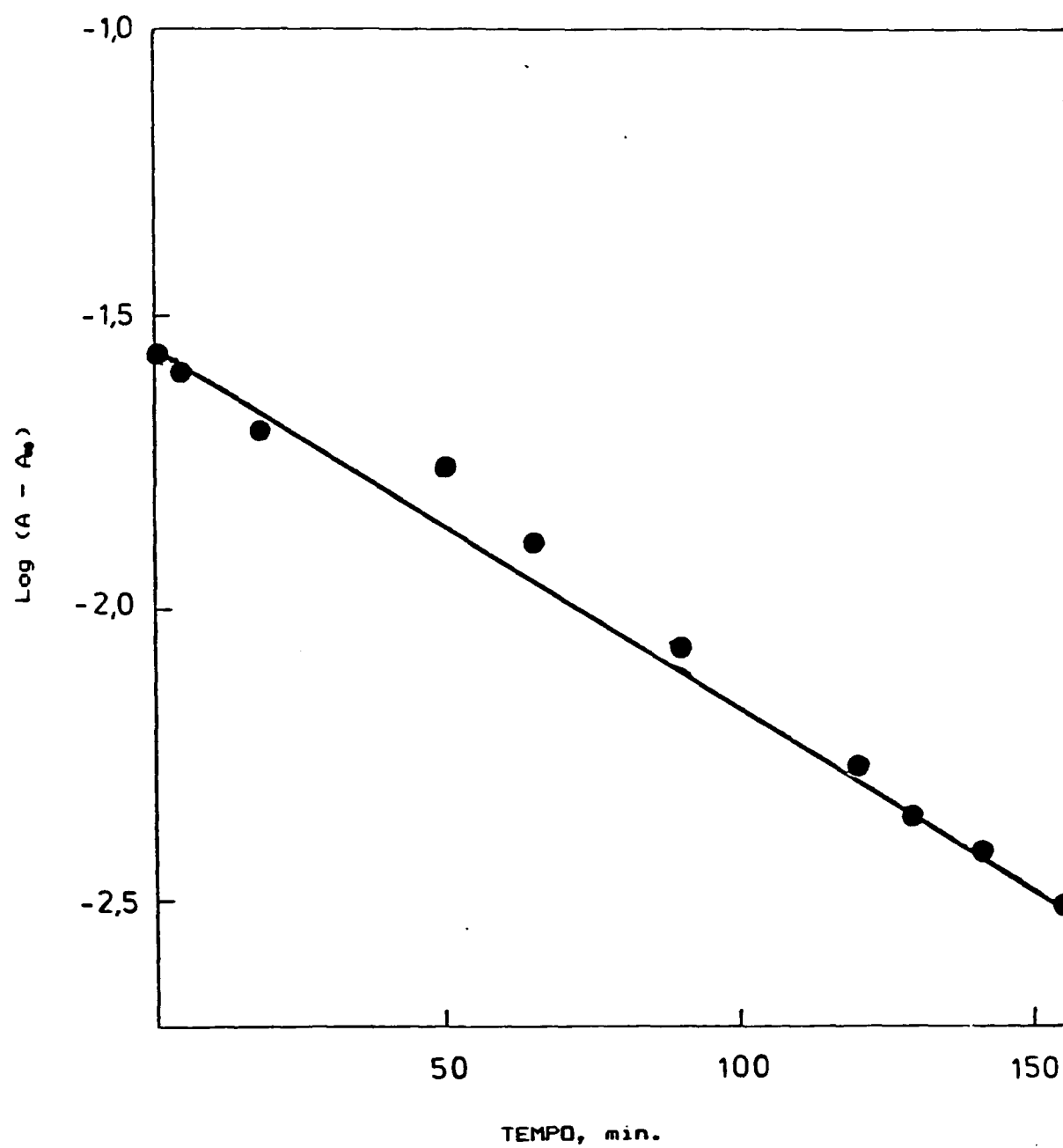


Fig. 5a

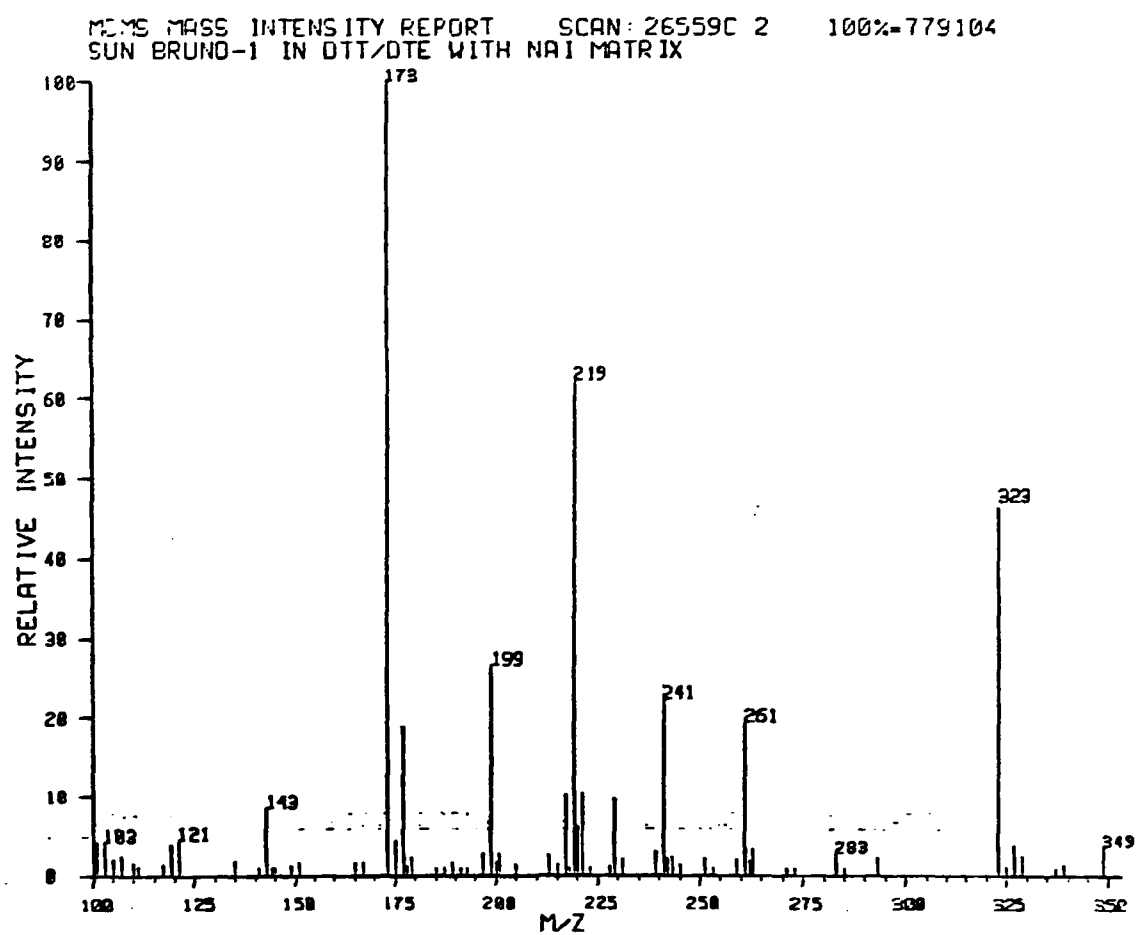
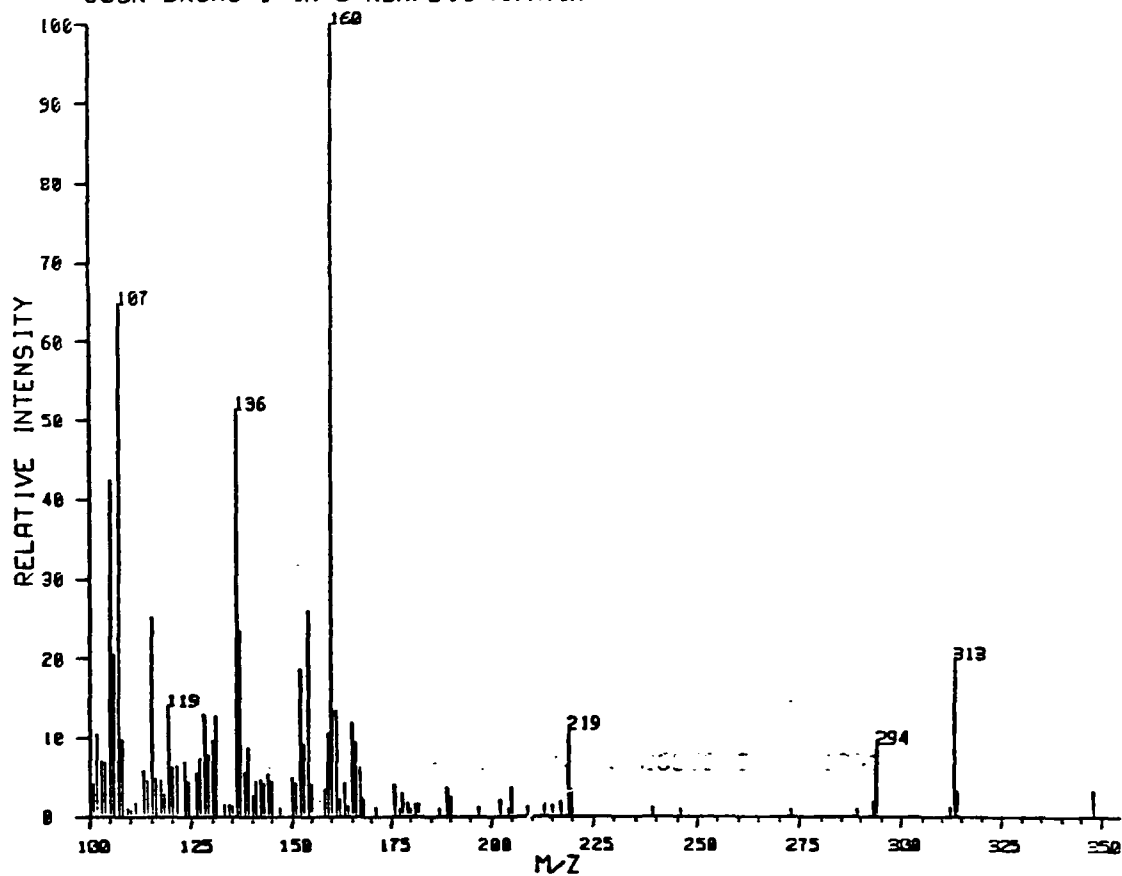


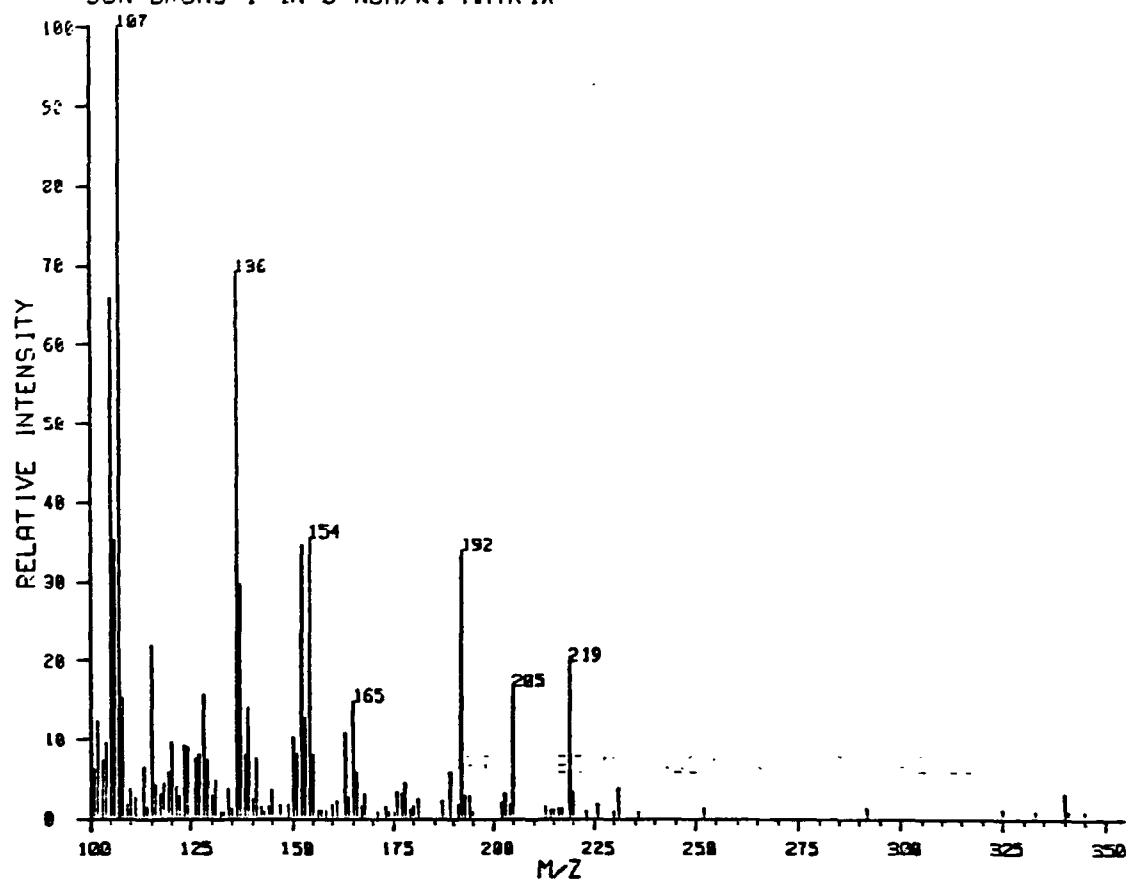
Fig. 5b

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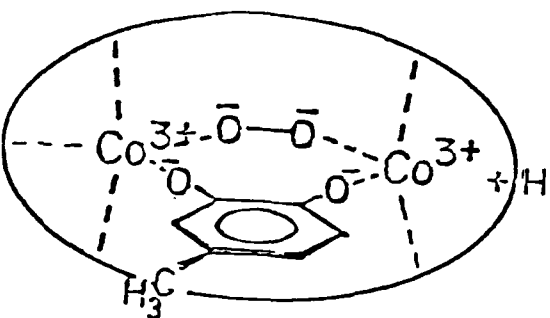
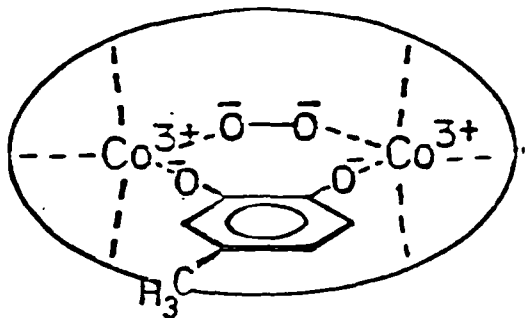
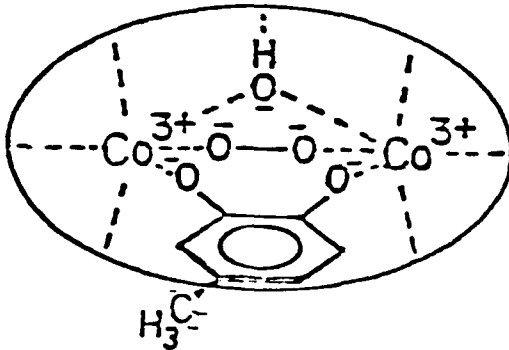
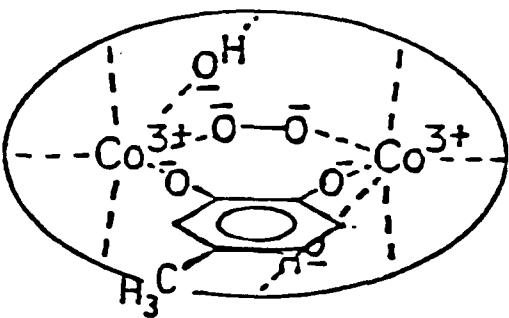
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SUN BRUNO-1 IN 3-NBA/KI MATRIX



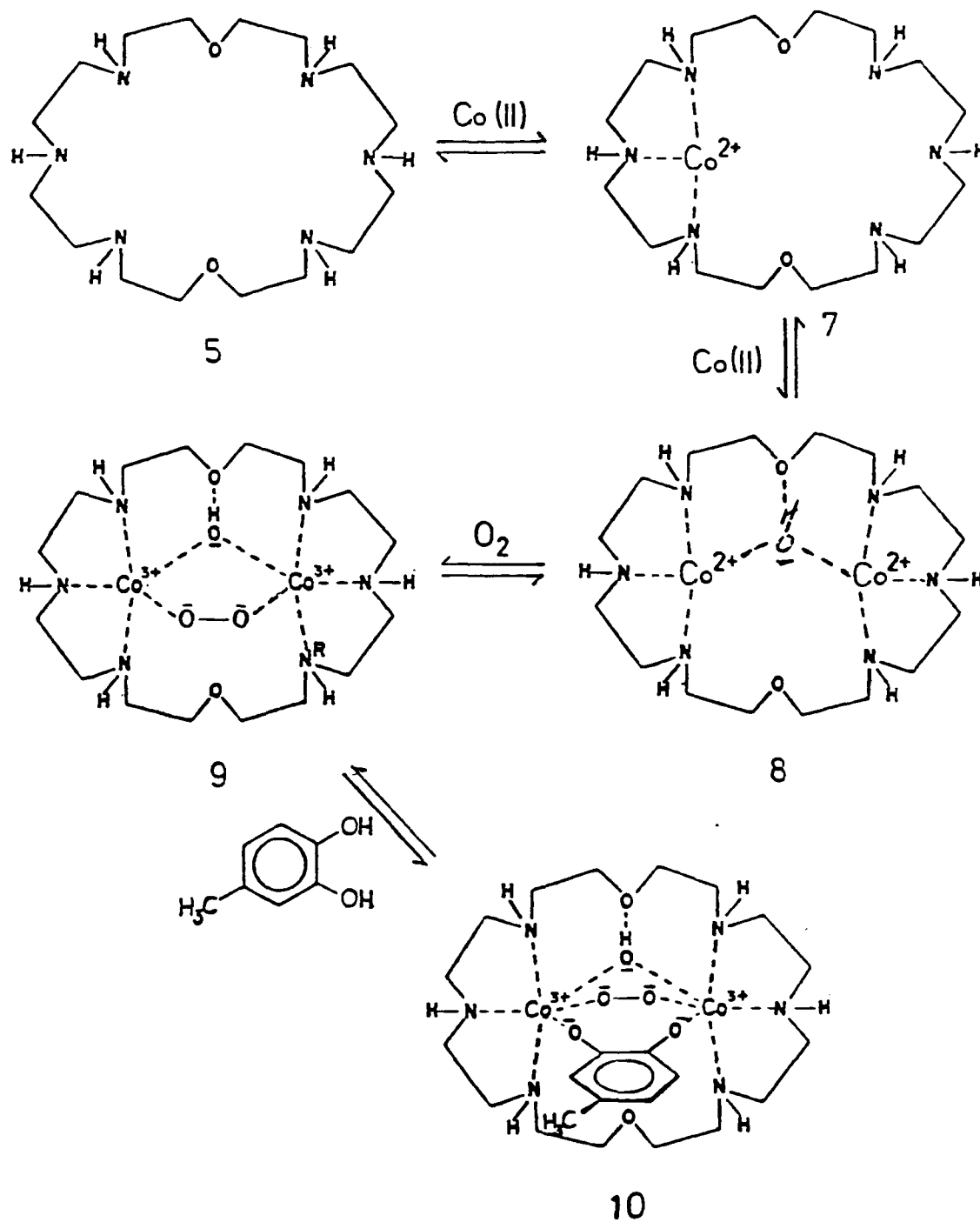
**Table 1.** Observed rate constants for degradation of 4-methylcatechol-bridged binuclear Co(II)-BISDIEN dioxygen complexes at 50.0 °C and  $\mu\text{C}$  and  $\mu = 0.100 \text{ M}$  (KCl)

pH	$k_{\text{obs}}, \text{min}^{-2}$
10.14	$6.0 \times 10^{-3}$
9.56	$6.3 \times 10^{-3}$
8.15	$6.2 \times 10^{-3}$
7.70	$5.4 \times 10^{-3}$

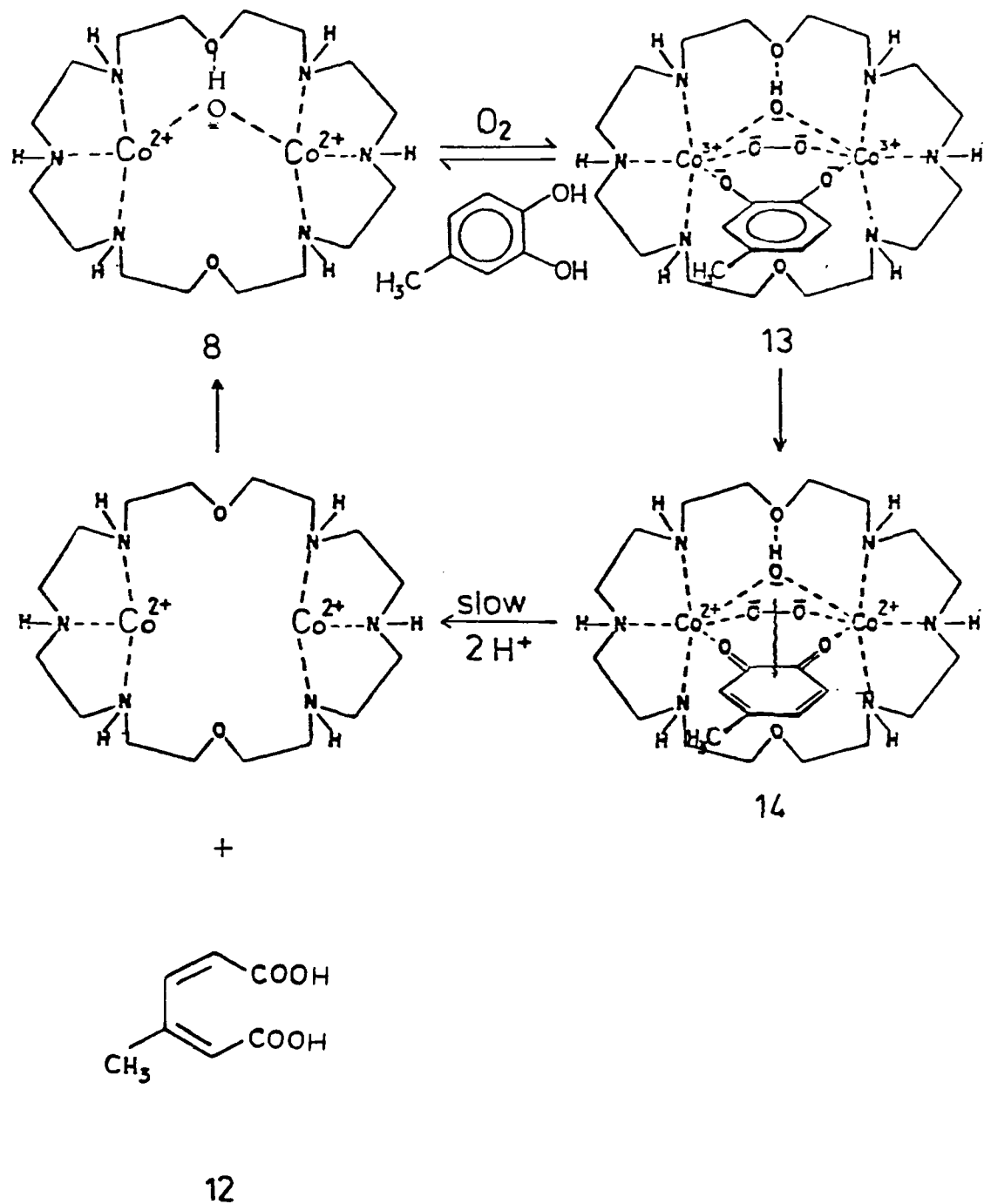
**Table II.** Specific rate constants for degradation of 4-methylcatechol-bridged binuclear Co(II)-BISDIEN dioxygen complexes at 50.0 °C and  $\mu = 0.100$  M (KCl)

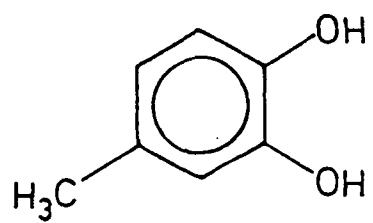
Species	$k, \text{min}^{-1}$
	$5,7 \times 10^{-3}$
	$8,3 \times 10^{-3}$
	$7,3 \times 10^{-3}$
	$6,1 \times 10^{-3}$

**Scheme I.** Formation of  $(\mu\text{-hydroxo})(\mu\text{-4-methylcatechol})(\mu\text{-peroxodicobalt(II)})\text{-BISDIEN}$ , **10**, where the complex  $(\mu\text{-hydroxo})(\mu\text{-peroxo})\text{dicobalt(II)-BISDIEN}$ , **9**, is the *receptor* complex and 4-methylcatechol is the substrate.

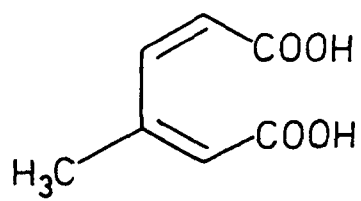


**Scheme II.** Proposed mechanism for the oxidation of 4-methylcatechol in the cavity of BISDIEN





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